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Cosmetic formulations and colorants for keratin fibers, used for cleaning and/or conditioning skin and hair and restructuring and coloring keratin fibers, especially human hair, contain complex of sericin and fibroin and/or derivatives

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Abstract of DE 10333253 (A1)

Cosmetic formulations contain a complex (A) of (A1) sericin, sericin hydrolyzate, their derivatives and/or mixtures and (A2) fibroin, its hydrolyzate, their derivatives and/or mixtures. - Independent claims are also included for the following: - (1) Colorant for keratin fibers containing dye precursor(s) (DP), complex (A) and an amphoteric polymer (AP) in a cosmetically acceptable vehicle; - (2) 2-component colorant with DP in a first component, A in a second component and AP in one or both components; - (3) similar colorant with a third component that contains oxidant(s).

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[0001] The present invention concerns hair coloring means, which contain a particular maintaining active substance combination, as well as a method to the coloration of keratinischer fibers using this active substance combination.

State of the art

[0002] Human hair becomes today in various manner with hair-cosmetic preparing treated. In addition belong for instance the purification of the hairs with shampoos, the care and regeneration with rinses and cures as well as to bleaches, dyeing and deforming of the hairs with coloring means, hue means, waving means and styling preparations. Agents play a prominent role to the change or Nuancierung of the color of the Kopfharees.

[0003] For durable, intense colorations with corresponding authenticity characteristics so called oxidation coloring means become used. Such coloring means contain usually oxidation coloring material before products, so called developer components and Kupplerkomponenten. The developer components train the bottom influence of oxidizing agents or of atmospheric oxygen among themselves or bottom clutch with or several Kupplerkomponenten the actual dyes. Frequent ones become also combinations from oxidation coloring materials and direct dyes to the achievement of particular nuances used. The oxidation coloring means are characterised by excellent, prolonged continuous coloring results.

[0004] For temporary colorations usually coloring or hue means becomes used, which contains so called Direktzieher as coloring component. Here it concerns dye molecules, which draw direct up on the hair and need no oxidative process for the formation of the color. To these dyes from the antiquity to the coloration of body and hairs known Henna for example already belongs. These colorations are usually sensitive against shampoo kidneys, so that a multiple undesirable nuance shift or a visible "discoloration" can occur. An other disadvantage of such temporary colorations lies in the fact justified that these colorations add themselves to the natural hair clay/tone in addition and make possible thus only nuances, which are darker as the output clay/tone. Therefore will also coloring means on basis of direktziehenden dyes frequent in combination with oxidizing agent preparing applied, in order to lighten beside the actual coloration the output colour of the fibers.

[0005] Both processes involve therefore the use of strong oxidizing agents as for example hydrogen peroxide solutions. Perhaps this can damage that hair which can be colored. These damages must then with corresponding care products counteracted become.

[0006] It is for a long time conventional to submit the hairs of a particular post treatment. , Usually treated in form of a rinse, the hairs with particular active ingredients, for example quaternary ammonium salts or particular polymers become. Depending upon formulation combing barness, stop and filling of the hairs are improved by this treatment and the Splissrate reduced.

[0007] Further so called combined preparations became developed, in order to reduce the effort of the conventional multitstage methods, in particular with the direct application by consumers, in youngest time.

[0008] In case of the hair coloring means these preparations beside the ingredients conventional for these products contain additional active ingredients, which were reserved the early shedding oh treatment means. That consumer saves thus an application step.

[0009] It exists therefore further a need to active ingredients and/or effect often combinations with good maintaining properties and good biological degradable, is excluded with which undesirable Kumulationen on the hair.

[0010] Sought ones are in particular active ingredients, which are in the layer, the internal structure of fibers, in particular keratinischer fibers to improve significant. Bottom structure stabilization, thus restructuring in the sense of the invention, a reduction of the damages of keratinischer fibers resulted from most different influences is to be understood. Here for example the restoration of the natural strength plays a substantial role.

Restrukturierte fibers are characterised for example by an improved glossiness or by an improved grasp or by an easier combing barness. Additional one wise it an optimized strength and elasticity up. A successful restructuring can be proven to physical as melting point increase in the comparison to the damaged fiber. The ever high melting point of the hair is, the more solid is the structure of the fiber. A detailed description of the method to the determination of the melting range of hairs is in the DE 196,173 95 A1.

[0011] Protein hydrolysates actual and their use in cosmetic agents are already for a long time known. For this is referred, for example to the pertinent technical literature in A. Domsch, "the cosmetic preparations", band II, page 205 and the subsequent, publishing house for the chemical industry, H. Ziolkowski. It is however no reference on a restructuring, which is characterised by an increased strength and an elasticity to find.

[0012] It is already for a long time known to begin in cosmetic preparations of proteins or modified proteins to the achievement of maintaining effects. For this purpose either water-soluble proteins become or by chemical and/or by enzymatic reactions modified, thus water-soluble made proteins used. Straight one with the conversions to the achievement of a sufficient water solubility is with Faserproteinen a frequent so large degradation required that the cosmetic efficacy is sufficient no longer.

[0013] A cosmetic very interesting Faserprotein is silk. Bottom silk understands one the fibers of the Kokons of the Maulbeer Seidenspinner (Bombyx mori L.). The crude silk fiber consists of a double thread Fibroin. As cement substance Sericin holds this double thread together. Silk consists to 70-80 Gew.% of Fibroin, 19-28 Gew.% Sericin, 0.5-1 Gew.% of fat and 0.5-1 Gew.% of dyes and inorganic ingredients.

[0014] The essential ingredients of the Sericin are with approx. 46 Gew.% Hydroxyamino-säuren. The Sericin consists of a group of 5 to 6 proteins. The substantial amino acids of the Sericines are serine (Ser, 37 Gew.%), aspartate (Asp, 26 Gew.%), glycine (Gly, 17 Gew.%), alanine (Ala), leucine (Leu) and tyrosine (Tyr).

[0015] The water-insoluble Fibroin is to be ranked among the Skleroproteinen with langkettiger molecular structure. The major constituents Fibroin are glycine (44 Gew.%), alanine (26 Gew.%), and tyrosine (13 Gew.%). An other substantial structure characteristic of the Fibroinoes is the Hexapeptidsequenz Ser Gly Ala Gly Ala Gly.

[0016] Technical one is it easily and manner possible to separate the two silk proteins. Thus it does not surprise that both Sericin and Fibroin and raw materials alone known to the use in cosmetic products for itself in each

case are. Further protein hydrolysates are and - derivatives on the basis of the single in each case silk proteins of known raw materials in cosmetic agents. Thus for example Sericin becomes as such on the part of the companies Pentapharm Ltd. as commercial product with the designation Sericin code 303-02 sold. Fibroin by far more frequent still becomes offered as protein hydrolysate with different molecular weights in the market. These hydrolysates become in particular sold as "Seidenhydrolysate". Thus becomes the for example bottom trade name Promois- (R) > Silk hydrolyzed Fibroin with average molecular weights between 350 and 1000 sold. Also in the DE 31 39 438 A1 colloidal Fibroinlösungen becomes described as addition in cosmetic agents.

[0017] The positive properties of the silk protein derivatives from Sericin and Fibroin are in each case known for itself taken in the literature. Thus the sales brochure of the companies describes Pentapharm the cosmetic effects of the Sericines on the skin as reizlindernd, hydrated-end and film-formed. The properties of a shampoo contained Sericin as maintaining component become in the "medical Kosmetologie 17, 91-110 (1987)" from W. Angel et al. reported. The effect of a Fibroinderivates becomes for example described in the DE 31 39 438 A1 as maintaining and avivierend for the hair.

Object

[0018] It now surprisingly found that keratinische fibers, which become colored with preparing contain the Sericin and Fibroin and/or their derivatives in combination with particular polymers, significant increased properties exhibit.

[0019] A first subject-matter of the present invention are therefore agents to the coloration of keratinischer fibers, those in a cosmetic acceptable carrier

- at least one coloring material before product (FV),
 - an active substance complex (A), existing
 - from an active ingredient (A1), which selected is from Sericin and/or Sericinhydrolysaten and/or their derivatives and/or their mixtures, and
 - an active ingredient (a2), which selected is from Fibroin and/or its hydrolysates and/or their derivatives and/or mixtures from it, as well as
 - an amphoteric polymer (AP)
- contained.

[0020] The combination according to invention from active substance complex the significant substantial inner and outside structure characteristics represented before and the strength as well as the elasticity of human hairs improves (A) and amphoteric polymer (AP).

[0021] According to invention used can become as active ingredients (A1) in the active substance complex (A):

- native Sericin,
- hydrolyzed and/or other derivatized Sericin, as for example commercial products with the INCI - designations Sericin, Hydrolyzed Sericin, or Hydrolyzed Silk,
- mixture from amino acids serine, aspartate and glycine and/or their methyl, Propyl, ISO Propyl, Butyl, ISO butyl ester, whose salts as for example hydrochlorides, sulfates, acetates, citrates, tartrates, whereby in this mixture the serine and/or its derivatives are contained to 20 to 60 Gew.%, the aspartate and/or its derivatives to 10-40 Gew.%, and the glycine and/or its derivatives to 5 to 30 Gew.%, under the condition that the amounts of these amino acids and/or their derivatives preferably complement each other to 100 Gew.%,
- as well as their mixtures.

[0022] According to invention used can become as active ingredients (a2) in the active substance complex (A):

- native Fibroin transferred into a soluble form,
- hydrolyzed and/or other derivatized Fibroin, particularly part-hydrolyzed Fibroin, which contains the amino acid sequence Ser Gly Ala Gly Ala Gly as major constituent,
- the amino acid sequence Ser Gly Ala Gly Ala Gly,
- mixture amino acids glycine, alanine and tyrosine and/or their methyl, Propyl, ISO Propyl, Butyl, ISO butyl ester, whose salts as for example hydrochlorides, sulfates, acetates, citrates, tartrates, whereby in this mixture the glycine and/or its derivatives are contained in amounts of 20-60 Gew.%, the alanine and its derivatives in amounts of 10-40 Gew.%, and the tyrosine and its derivatives in amounts from 0 to 25 Gew.%, under the condition that the amounts of these amino acids and/or their derivatives preferably complement each other to 100 Gew.%,
- as well as their mixtures.

[0023] It can be preferred according to invention that one of the two active substance components of the active substance complex becomes (A) in the native or if necessary soluble made form used. It is according to invention also possible to use a mixture from several active ingredients (A).

[0024] It can be preferred according to invention that the two active ingredients (A1) and (a2) become particularly according to invention used in the ratio from 10:90 to 70:30, in particular 15:85 to 50:50 and whole 20:80 to 40:60 related to their respective contents of active active substance in the preparing.

[0025] The derivatives of the hydrolysates of Sericin and Fibroin cover both anionic and kationisierte protein hydrolysates. The protein hydrolysates according to invention of Sericin and Fibroin as well as the derivatives prepared from it can become from the corresponding proteins by a chemical, in particular alkaline or acid hydrolysis, by an enzymatic hydrolysis and/or a combination from both kinds of hydrolysis recovered. The hydrolysis of proteins usually results in a protein hydrolysate with a molecular weight distribution of approximately 100 Dalton up to several thousand Dalton. Preferred ones are such protein hydrolysates of Sericin and Fibroin and/or their derivatives, whose at the basis located protein portion exhibits a molecular weight of 100 up to 25000 Dalton, preferred 250 to 10000 Dalton. Further bottom cationic protein hydrolysates about Sericin and Fibroin amino acids also quaternierte and their mixtures are to be understood. The Quaternisierung of the protein hydrolysates or the amino acids becomes frequent by means of quaternären ammonium salts as for example N, N-Dimethyl-n (n-alkyl) - n (2-hydroxy-3-chloro-n-propyl) - ammonium halides performed. Further

the cationic protein hydrolysates can be also still other derivatized. As typical examples for the cationic protein hydrolysates according to invention and - derivatives are those the bottom INCI - designations in the "international Cosmetic ingredient Dictionary and Handbook", (seventh edition 1997, The Cosmetic, Toiletry, and ask-climbs Association 1101 17< th> Street, N.W., Suite 300, Washington, DC 20036-4702) and in the trade of available products mentioned mentioned: Cocodimonium hydroxypropyl Hydrolyzed Silk, Cocodimonium hydroxypropyl Silk Amino Acids, Hydroxypropyltrimonium Hydrolyzed Silk, Laurylidimonium hydroxypropyl Hydrolyzed Silk, Steardimonium hydroxypropyl Hydrolyzed Silk, Quaternium-79 Hydrolyzed Silk. As typical examples for the anionic protein hydrolysates according to invention and - derivatives are those the bottom INCI designations in the "international Cosmetic ingredient Dictionary and Handbook", (seventh edition 1997, The Cosmetic, Toiletry, and ask-climbs Association 1101 17< th> Street, N.W., Suite 300, Washington, DC 20036-4702) and in the trade of available products mentioned mentioned: Potassium Cocoyl Hydrolyzed Silk, Sodium Lauroyl Hydrolyzed Silk or Sodium Stearoyl Hydrolyzed Silk. In the long run those are still the bottom INCI designations in the trade available products mentioned as typical examples for insertable the according to invention derivatives from Sericin and Fibroin: Ethyl ester OF Hydrolyzed Silk and Hydrolyzed Silk PG-Propyl Methylsilanediol. More useful further according to invention, although not necessarily preferred are in the trade the available products with the INCI - designations palmitoyls of oligopeptides, palmitoyl Pentapeptide-3, palmitoyl Pentapeptide-2, acetyl Hexapeptide-1, acetyl Hexapeptide-3, copilot by Tripeptide-1, Hexapeptide-1, Hexapeptide-2, MEA hydrolyzed Silk.

[0026] In the agents according to invention the active substance complex is (A) in amounts of 0,001-10 Gew. - % related to the entire agent contain. Amounts from 0,001 to 5 Gew. - %, in particular 0.005 to 1 Gew. - %, are whole particularly preferred.

[0027] Further the agents according to invention contain beside of active substance complex (A) at least an amphoteric polymer (AP) used become. The bottom term of amphoteric polymers both such polymers, which in the molecule both free amino group and free - COOH or SO₃H-Gruppen contained and to the formation of inner salts capable is, and zwitterionic polymers, which in the molecule quaternary ammonium groups and, become according to invention - COO< -> - or - SO₃< -> - groups contain, and such polymers summarized, which - COOH or SO₃H-Gruppen and quaternary ammonium groups contain.

[0028] Examples for insertable according to invention Amphopolymer are for example those the bottom designation Amphomer< (R)-> available commercial products of the company National Starck. As typical members are copolymers from third. - Butylaminoethylmethacrylat, n (1,1,3,3-Tetramethylbutyl) acrylamide as well as two or several monomers from the group acrylic acid, methacrylic acid and their simple esters mentioned, those the INCI designation Octylacrylamid/ Acrylates/Butylaminoethylmethacrylat copolymer inertial. Into this group fall for example the commercial products Amphomer< (R)> 028-4910 as well as Amphomer< (R)> LV 71. Furthermore still the commercial product is Amphomer< (R)> Numerical control (INCI designation: Acrylates/Octylacrylamide copolymer) mentioned.

[0029] Other insertable according to invention amphoteric polymers are in the British Patent Laid open 2 the, 104,091, the European Patent Laid open 47,714, the European Patent Laid open 217,274, the European Patent Laid open 283,817 and the German Patent Laid open 28 17 369 compounds specified.

[0030] Preferred used amphoteric polymers are such polymers, essentially build themselves up out

(A) Monomers with quaternary ammonium groups of the general formula (I),
 $R_1 > 1 - CH=CR_2 > 2 - CO-Z (CnH2n) - N_1 < (+) > R_3 > 3 - R_4 > 4 - R_5 > 5 - A_1 < (-) > (I)$
 in $R_1 > 1$ and $R_2 > 2$ independently R 4 stand for hydrogen or a methyl group< and> a $R_3 < , >$ and $R_4 < 5 >$ independently for alkyl groups with 1 to 4 carbon atoms, Z a NH group or an oxygen atom, n a whole number from 2 to 5 and $A_1 < (-) >$ the anion of an organic or inorganic acid one is, and
 (B) monomers carbonic acids of the general formula (II),
 $R_6 > 6 - CH=CR_7 > 7 - COOH (II)$
 in those $R_6 > 6$ and $R_7 > 7$ hydrogen or methyl groups is independent.

[0031] These compounds can become both direct and in salt form, which becomes obtained by neutralization of the polymers, for example with an alkali hydroxide, used according to invention. Concerning the details of the preparation of these polymers expressly respect taken becomes on the content of the German Patent Laid open 39 29 973. Whole particularly preferred is such polymers, with which monomers of the type become (A) used, with those $R_3 > 3$, $R_4 > 4$ and $R_5 < 5 >$ Methyl groups are. Further monomers of the type (A) preferred can be, with those Z for a NH group stand. Furthermore the anion A stands< (-) > with the monomers of the type (A) preferred for a halide, a Methoxysulfat or an Ethoxysulfat ion; Acrylamidopropyl trimethylammoniumchlorid is particularly preferred monomer (A). As monomer (B) for the polymers mentioned preferred acrylic acid becomes used.

[0032] The amphoteric polymers become in the agents according to invention preferred in amounts from 0,001 to 5 Gew. - % used. Particularly preferred is amounts of 0,1 to 3 Gew. - %. The quantity specifications are in each case related to the coloring preparation, i.e. if necessary on the mixture from the actual coloring cream and the care component, without the if necessary used oxidizing agent preparation.

[0033] Regarding in the coloring means according to invention insertable other coloring often before products (FV) is not subject the present invention to any limitations. The coloring means according to invention can as coloring material before products

- Oxidation coloring material before products of the developer and/or Kuppler type, and
- Preliminary stages of nature-analogue dyes, like indol and Indolin derivatives, as well as mixtures of members of these groups contain.

[0034] In the frame the agents according to invention contain at least one coloring material before product of the developer and/or Kupplertyp of a first preferred embodiment of the present invention.

[0035] As developer components become usually primary aromatic amines with an other, in para or ortho position located, free or substituted hydraulic XY or amino group, Diaminopyridinderivate, heterocyclic hydrazones, 4-Aminopyrazolderivate as well as 2,4,5,6-Tetraaminopyrimidin and its derivatives used.

[0036] It can be preferred according to invention, as developer component a p-Phenylendiaminderivat or begin a one of its physiological acceptable salts. Particularly preferred is p-Phenylendiaminderivate of the formula (E1)

EMI9.1

how

- Gc 1> stands for an hydrogen atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest, for one (c1 to C4) - Alkoxy (c1 to C4) - alkyl residue, 4'- - Aminophenylrest or a c1 to C4-Alkylrest, which with a nitrogenous group, a phenyl or 4'- - Aminophenylrest a substituted is;

- Gc 2> stands for an hydrogen atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest, for one (c1 to C4) - Alkoxy (c1 to C4) - alkyl residue or a c1 to C4-Alkylrest, which is substituted with a nitrogenous group;

- Gc 3> an halogen atom, like a chlorine, stands a bromine, an iodine or fluorine atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest, a c1 to C4-Hydroxyalkoxyrest, a c1 to C4-Acetylaminoalkoxyrest, a c1 to C4-Mesylaminoalkoxyrest or a c1 to C4-Carbamoylaminoalkoxyrest for an hydrogen atom;

- Gc 4> an halogen atom stands or a c1 to C4-Alkylrest or for an hydrogen atom,
- if Gc 3> and Gc 4> in ortho position, can they stand a common verb-moving [alpha], [omega] - for Alkylendioxygruppe to each other, as for example a Ethylendioxygruppe form.

[0037] Examples for according to invention the c1 to C4-Alkylreste, specified as substituents in the compounds, are the groups methyl, ethyl, Propyl, Isopropyl and Butyl. Ethyl and methyl are preferred alkyl radicals. Preferred according to invention c1 to C4-Alkoxyreste is for example a Methoxy or an ethoxy group. Further can become as preferable examples for a c1 to C4-Hydroxyalkylgruppe a Hydroxymethyl, a 2-Hydroxyethyl, a 3-Hydroxypropyl or a 4-Hydroxybutylgruppe mentioned. A 2-Hydroxyethylgruppe is particularly preferred. A particularly preferred C2 to C4-Polyhydroxyalkylgruppe is the 1,2-Dihydroxyethylgruppe. Examples for halogen atoms are I, Cl or Br- atoms. Cl- atoms are whole particularly preferred according to invention. The other used terms are derived according to invention from the definitions given here. Examples for nitrogenous groups of the formula (E1) are in particular the amino group, c1 to C4-Monoalkylaminogruppen, c1 to C4-Dialkylaminogruppen, c1 to C4-Trialkylaminiumgruppen, c1 to C4-Monohydroxyalkylaminogruppen, Imidazolium and ammonium.

[0038] Particularly preferred p-phenylene diamines of the formula (E1) are selected from p-phenylene diamine, p-Toluyldiamin, 2-Chlor-p-phenyldiamin, 2,3-Dimethyl-p-phenyldiamin, 2,6-Dimethyl-p-phenyldiamin, 2,6-Diethyl-p-phenyldiamin, 2,5-Dimethyl-p-phenyldiamin, N, N-Dimethyl-p-phenyldiamin, N, N-Diethyl-p-phenyldiamin, N, N-dipropyl-p-phenyldiamin, 4-Amino-3-methyl (N, N-diethyl) - aniline, N, N-Until ([beta] - hydroxyethyl) - p-phenyldiamin, 4-N, N-Until ([beta] - hydroxyethyl) - p-phenyldiamin, 4-N, N-Until (ss-hydroxyethyl) - amine CO2 chlorine aniline, 2 ([beta] - Hydroxyethyl) - p-phenyldiamin, 2 ([alpha], [beta] - Dihydroxyethyl) - p-phenyldiamin, 2-Fluor-p-phenyldiamin, 2-Isopropyl-p-phenyldiamin, n ([beta] - hydroxypropyl) - p-phenyldiamin, 2-Hydroxymethyl-p-phenyldiamin, N, N-Dimethyl-3-methyl-p-phenyldiamin, N, n (ethyl, [beta] - hydroxyethyl) - p-phenyldiamin, n ([beta], [gamma] - Dihydroxypropyl) - p-phenyldiamin, n (4' - Aminophenyl) - p-phenyldiamin, N-Phenyl-p-phenyldiamin, 2 ([beta] - Hydroxyethoxy) - p-phenyldiamin, 2 ([beta] - Acetylaminoethoxy) - p-phenyldiamin, n ([beta] - Methoxyethyl) - p-phenyldiamin and 5,8-Diaminobenzo-1,4-dioxan as well as their physiological acceptable salts.

[0039] Whole according to invention particularly preferred p-Phenylendiaminderivate of the formula (E1) is p-phenylene diamine, p-Toluyldiamin, 2 ([beta] - Hydroxyethyl) - p-phenyldiamin, 2 ([alpha], [beta] - Dihydroxyethyl) - p-phenyldiamin and N, N-Until ([beta] - hydroxyethyl) - p-phenyldiamin.

[0040] It can be further according to invention preferred to begin as developer component compounds which contain at least two aromatic nucleuses, which are substituted with revision modification NO and/or hydroxyl groups.

[0041] The bottom two-fulls of seeds developer components, which in the coloring compositions according to the invention used to become to be able, one can call in particular the compounds, which correspond to the subsequent formula (E2), as well as their physiological acceptable salts:

EMI11.1

where:

- Zc 1> and Zc 2> stand independently for a hydroxyl or a NH2-Rest, which is by a c1 to C4-Alkylrest, by a c1 to C4-Hydroxyalkylrest and/or by a verb moving Y substituted or if necessary it that if necessary part of a verb-moving ring system,

- the verb moving Y stands for several nitrogenous groups and/or several Heteroatomen such as oxygen, sulfur or nitrogen atoms an interrupted or terminated for an alkylene group with 1 to 14 carbon atoms, as for example a linear or branched alkylene chain or an alkyl ring, those of or being can and eventual by or several hydroxyl or c1 to C8-Alkoxyreste a substituted be can, or a direct bond,

- Gc 5> and Gc 6> stands independently for a hydrogen or an halogen atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4 Polyhydroxyalkylrest, a c1 to C4-Aminoalkylrest or a direct connection to the verb moving Y,

- Gc 7>, Gc 8>, Gc 9>, Gc 10>, Gc 11> and Gc 12> it stands independently for an hydrogen atom, a direct bond to the verb moving Y or a c1 to C4-Alkylrest, with the measure gifts that

- the compounds of the formula (E2) only a verb moving Y per molecule contain and

- the compounds of the formula (E2) at least an amino group contain, which carries at least an hydrogen atom.

[0042] The substituents used in formula (E2) are analogue according to invention defined to the above embodiments.

[0043] Preferred two-tull of seeds developer components of the formula (E2) are in particular:

N, N' until ([beta] - hydroxyethyl) - N, N' to (4' - aminophenyl) - 1,3-diamino-propan-2-ol, N, N' until ([beta] - hydroxyethyl) - N, N' to (4' - aminophenyl) - ethyl diamine, N, N' until (4-aminophenyl) - tetramethyldiamin,

N, N' until ([beta] - hydroxyethyl) - N, N' to (4-aminophenyl) - tetramethylenediamin, N, N' until (4-methylaminophenyl) - tetramethylenediamin, N, N' Diethyl n, N' to (4' - amino-3' methylphenyl) - ethyl diamine, until (2-hydroxy-5-aminophenyl) - methane, 1,3-Bis (2,5-diaminophenoxy) - Propan-2-ol, N, N' until (4' - aminophenyl) - 1,4-diazacycloheptan, N, N' until (2-hydroxy-5-aminobenzyl) - piperazin, n (4' - Aminophenyl) - p-phenylenediamin and 1,10-Bis (2', 5' - diaminophenyl) - 1,4,7,10-tetraoxadecan and their physiological acceptable salts.

[0044] Whole particularly preferred two-full of seeds developer components of the formula (E2) are N, N' until ([beta] - hydroxyethyl) - N, N' to (4' - aminophenyl) - 1,3-diamino-propan-2-ol, until (2-hydroxy-5-aminophenyl) - methane, 1,3-Bis (2,5-diaminophenoxy) - propan-2-ol, N, N' until (4' - aminophenyl) - 1,4-diazacycloheptan and 1,10-Bis (2', 5' - diaminophenyl) - 1,4,7,10-tetraoxadecan or one of their physiological acceptable salts.

[0045] Further it can be preferred according to invention, as developer component a p-Aminophenolderivat or begin a one of its physiological acceptable salts. Particularly preferred is p-Aminophenolderivate of the formula (E3)

EMI 13.1

where:

- G< 13> an halogen atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest, stands for one (c1 to C4) - Alkoxy (c1 to C4) for an hydrogen atom, - alkyl residue, a c1 to C4-Aminoalkylrest, a hydraulic XY (c1 to C4) - alkylaminorest, a c1 to C4-Hydroxyalkylrest, a c1 to C4-Hydroxyalkyl (C1-bis C4) - aminoalkylrest or one (the c1 to C4-Alkylamino) - (c1 to C4) alkyl residue, and

- G< 14> a hydrogen or an halogen atom, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest stands, for one (c1 to C4) - Alkoxy (c1 to C4) for - alkyl residue, a c1 to C4-Aminoalkylrest or a c1 to C4-Cyanoalkylrest,

- G< 15> stands for hydrogen, a c1 to C4-Alkylrest, a c1 to C4-Monohydroxyalkylrest, a C2 up to C4-Polyhydroxyalkylrest, a Phenylrest or a benzyle remainder, and

- G< 16> an halogen atom stands for hydrogen or.

[0046] The substituents used in formula (E3) are analogue according to invention defined to the above embodiments.

[0047] Preferred p-Aminophenole of the formula (E3) is in particular p-aminophenol, N-methyl-p-aminophenol, 4-Amino-3-methyl-phenol, 4-Amino-3-fluorphenol, 2-Hydroxymethylamino-4-aminophenol, 4-Amino-3-hydroxymethylphenol, 4-Amino-2 (-hydroxyethoxy) - phenol, 4-Amino-2-methylphenol, 4-Amino-2-hydroxymethylphenol, 4-Amino-2-methoxymethyl-phenol, 4-Amino-2-aminomethylphenol, 4-Amino-2 ([beta] - hydroxyethyl aminomethyl) - phenol, 4-Amino-2 ([alpha], [beta] - dihydroxyethyl) - phenol, 4-Amino-2-fluorphenol, 4-Amino-2-chlorphenol, 4-Amino-2,6-dichlorphenol, 4-Amino-2 (diethylaminomethyl) - phenol as well as their physiological acceptable salts.

[0048] Whole particularly preferred compounds of the formula (E3) are p-aminophenol, 4-Amino-3-methylphenol, 4-Amino-2-aminomethylphenol, 4-Amino-2 ([alpha], [beta] - dihydroxyethyl) - phenol and 4-Amino-2 (diethyl aminomethyl) - phenol.

[0049] Furthermore the developer component can be selected from o-aminophenols and its derivatives, as for example 2-Amino-4-methylphenol, 2-Amino-5-methylphenol or 2-Amino-4-chlorphenol.

[0050] Further the developer component can be selected from heterocyclic developer components, as for example the Pyridin, Pyrimidin, Pyrazol, Pyrazol Pyrimidin derivatives and their physiological acceptable salts.

[0051] Preferred Pyridin derivatives are in particular the compounds, which become in the patents GB 1,026,978 and GB 1,153,196 described, like 2,5-Diamino-pyridin, 2 (4' - Methoxyphenyl) - amino-3-amino-pyridin, 2,3-Diamino-6-methoxy-pyridin, 2 ([beta] - Methoxyethyl) - amino-3-amino-6-methoxy-pyridin and 3,4-Diamino-pyridin.

[0052] Preferred Pyrimidin derivatives are in particular the compounds, which in the German patent DE 2,359,399, which Japanese Patent Laid open JP 02019576 a2 or in the Patent Laid open WHERE 96/15765 described become, like 2,4,5,6-Tetraaminopyrimidin, 4-Hydroxy-2,5,6-triaminopyrimidin, 2-Hydroxy-4,5,6-triaminopyrimidin, 2-Dimethylamino-4,5,6-triaminopyrimidin, 2,4-Dihydroxy-5,6-diaminopyrimidin and 2,5,6-Triaminopyrimidin.

[0053] Preferred Pyrazol derivative are in particular compounds, which in the patents DE 3,843,892, DE 4,133,957 and patent applications WHERE 94/08969, WHERE 94/08970, EP-740 931 and DE 195 43 988 described become, like 4,5-Diamino-1-methylpyrazol, 4,5-Diamino-1 ([beta] - hydroxyethyl) - pyrazol, 3,4-Diaminopyrazol, 4,5-Diamino-1 (4' - chlorine benzyle) - pyrazol, 4,5-Diamino-1,3-dimethylpyrazol, 4,5-Diamino-3-methyl-1-phenylpyrazol, 4,5-Diamino-1-methyl-3-phenylpyrazol, 4-Amino-1,3-dimethyl-5-hydrazinopyrazol, 1-Benzyl-4,5-diamino-3-methylpyrazol, 4,5-Diamino-3-tert. - butyl-1-methylpyrazol, 4,5-Diamino-1-tert. - butyl-3-methylpyrazol, 4,5-Diamino-1 ([beta] - hydroxyethyl) - 3-methylpyrazol, 4,5-Diamino-1-ethyl-3-methylpyrazol, 4,5-Diamino-1-ethyl-3 (4' - methoxyphenyl) - pyrazol, 4,5-Diamino-1-ethyl-3-hydroxymethylpyrazol, 4,5-Diamino-3-hydroxymethyl-1-methylpyrazol, 4,5-Diamino-3-hydroxymethyl-1-isopropylpyrazol, 4,5-Diamino-3-methyl-1-isopropylpyrazol, 4-Amino-5 ([beta] - aminoethyl) - amino-1,3-dimethylpyrazol, 3,4,5-Triaminopyrazol, 1-Methyl-3,4,5-triaminopyrazol, 3,5-Diamino-1-methyl-4-methylaminopyrazol and 3,5-Diamino-4 ([beta] - hydroxyethyl) - amino-1-methylpyrazol.

[0054] Preferred Pyrazol Pyrimidin derivatives are in particular the derivatives of the Pyrazol [1,5-a] - pyrimidin the subsequent formula (E4) and its tautomeren forms, if a tautomeres balance exists:

EMI 15.1

where:

- G< 17>, G< 18>, G< 19> and G< 20> independently stand for an hydrogen atom, a c1 to C4-Alkylrest, an aryl residue, a c1 to C4-Hydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest for one (c1 to C4) - Alkoxy (c1 to C4) - alkyl residue, a c1 to C4-Aminoalkylrest, which can be protected by an acetyl ureide or a sulphonyl remainder if

necessary, one (c1 to C4) - alkyl revision modification NO (c1 to C4) - alkyl residue, a the [(c1 to C4) - alkyl] - (c1 to C4) - aminoalkylrest, whereby the dialkyl remainders if necessary form a carbon cycle or a hetero cycle with 5 or 6 chain links, a c1 to C4-Hydroxyalkyl or a the (c1 to C4) - [Hydroxyalkyl] - (c1 to C4) - aminoalkylrest, - the X-remainders stand independently for a hydrogen atom, a c1 to C4-Alkylrest, an aryl residue, a c1 to C4-Hydroxyalkylrest, a C2 to C4-Polyhydroxyalkylrest, a c1 to C4-Aminoalkylrest, for one (c1 to C4) - alkyl revision modification NO (c1 to C4) - alkyl residue, a the [(c1 to C4) alkyl] - (c1 to C4) - aminoalkylrest, whereby the dialkyl remainders if necessary form a carbon cycle or a hetero cycle with 5 or 6 chain links, a c1 to C4-Hydroxyalkyl or a the (c1 to C4-hydroxyalkyl) - it aminoalkylrest, an amino group, a c1 to C4-Alkyl or the (c1 to C4-hydroxyalkyl) -, an halogen atom, a group of carboxylic acid aminores or a sulfonic acid group,

- i has the value 0, 1, 2 or 3,

- p has the value 0 or 1,

- q has the value 0 or 1 and

- n has the value 0 or 1,

under the condition that

- is the sum from p + q unequal 0,

- if p + q same 2 is, n the value 0 has, and the groups NG< 17> G< 18> and NG< 19> G< 20> occupy the positions (2,3); (5,6); (6,7); (3,5) or (3,7);

- if p + q same 1 is, n the value 1 has, and the groups NG< 17> G< 18> (or NG< 19> G< 20>) and the positions (2,3) occupy the group OH; (5,6); (6,7); (3,5) or (3,7);

[0055] The substituents used in formula (E4) are analogue according to invention defined to the above embodiments.

[0056] If the Pyrazol [1,5-a] - pyrimidin an hydroxy group at one of the positions 2, 5 or 7 of the ring system of the above formula (E4) contains, exists a tautomeres balance, which becomes the example in the following scheme shown:

EMI 16.1

[0057] The bottom Pyrazol [1,5-a] - the above formula (E4) can one pyrimidinen call in particular:

- Pyrazol [1,5-a] - pyrimidin-3,7-diamin;

- 2,5-Dimethyl-pyrazol [1,5-a] - pyrimidin-3,7-diamin;

- Pyrazol [1,5-a] - pyrimidin-3,5-diamin;

- 2,7-Dimethyl-pyrazol [1,5-a] - pyrimidin-3,5-diamin;

- 3-Aminopyrazol [1,5-a] - pyrimidin-7-ol;

- 3-Aminopyrazol [1,5-a] - pyrimidin-5-ol;

- 2 (3-Aminopyrazol [1,5-a] - pyrimidin-7-ylamino) - ethanol;

- 2 (7-Aminopyrazol [1,5-a] - pyrimidin-3-ylamino) - ethanol;

- 2 (3-Aminopyrazol [1,5-a] - pyrimidin-7-yl) - (2-hydroxy-ethyl) - amino] - ethanol;

- 2 (7-Aminopyrazol [1,5-a] - pyrimidin-3-yl) - (2-hydroxy-ethyl) - amino] - ethanol;

- 5,6-Dimethylpyrazol [1,5-a] - pyrimidin-3,7-diamin;

- 2,6-Dimethylpyrazol [1,5-a] - pyrimidin-3,7-diamin;

- 3-Amino-7-dimethylamino-2,5-dimethylpyrazol [1,5-a] - pyrimidin;

as well as their physiological acceptable salts and its tautomeren forms, if tautomers a balance is present.

[0058] The Pyrazol [1,5-a] - pyrimidine of the above formula (E4) can become as in the literature described by cyclization on the basis of a Aminopyrazol or from hydrazine prepared.

[0059] In an other preferred embodiment the coloring means according to invention contain at least a Kupplerkomponente.

[0060] As Kupplerkomponenten become usually m phenylene diamine derivatives, Naphthole, resorcinol and Resorcinderivate, pyrazolones and m-Aminophenolderivate used. As Kupplersubstanzen are suitable in particular 1-Naphthol, 1,5, 2,7 - and 1,7-Dihydroxynaphthalin, 8-min CO2 methyl phenol, m-aminophenol, resorcinol, Resorcinmonomethylether, m phenylene diamine, 1-Phenyl-3-methyl-pyrazolon-5, 2,4-Dichlor-3-aminophenol, 1,3-Bis (2' , 4' - diaminophenoxy) - propane, 2-Chlor-resorcin, 4-Chlor-resorcin, 2-Chlor-6-methyl-3-aminophenol, 2-Amino-3-hydroxypyridin, 2-Methylresorcin, 5-Methylresorcin and 2-Methyl-4-chlor-5-aminophenol.

[0061] Preferred according to invention Kupplerkomponenten is

- M-aminophenols and its derivatives as for example 4'-amin CO2 methyl phenol, N-Cyclopentyl-3-aminophenol, 3-Amino-2-chlor-6-methylphenol, 2-Hydroxy-4-aminophenoxyethanol, 2,6-Dimethyl-3-aminophenol, 3-Trifluoroacetylaminol-2-chlor-6-methylphenol, 5-Amino-4-chlor-2-methylphenol, 5-Amino-4-methoxy-2-methylphenol, 5 (2' - Hydroxyethyl) - amine CO2 methyl phenol, 3 (Diethylamino) - phenol, N-Cyclopentyl-3-aminophenol, 1,3-Dihydroxy-5 (methylamino) - benzene, 3-Ethylamino-4-methylphenol and 2,4-Dichlor-3-aminophenol,

- O-aminophenols and its derivatives,

- M-Diaminobenzol and its derivatives as for example 2,4-Diaminophenoxyethanol, 1,3-Bis (2' , 4' - diaminophenoxy) - propane, 1-Methoxy-2-amino-4 (2' - hydroxyethylamino) benzene, 1,3-Bis (2' , 4' - diaminophenyl) - propane, 2,6-Bis (2' - hydroxyethylamino) - 1-methylbenzol and 1-Amino-3-bis (2' - hydroxyethyl) - aminobenzene,

- O-Diaminobenzol and its derivatives as for example 3,4-Diaminobenzoessäure and 2,3-Diamino-1-methylbenzol,

- And/ or Trihydroxybenzolderivate as for example resorcinol, Resorcinmonomethylether, 2-Methylresorcin, 5-Methylresorcin, 2,5-Dimethylresorcin, 2-Chlorresorcin, 4-Chlorresorcin, pyrogallol and 1,2,4-Trihydroxybenzol,

- Pyridinderivate as for example 2,6-Dihydroxypyridin, 2-Amino-3-hydroxypyridin, 2-Amino-5-chlor-3-hydroxypyridin, 3-Amino-2-methylamino-6-methoxypyridin, 2,6-Dihydroxy-3,4-dimethylpyridin, 2,6-Dihydroxy-4-methylpyridin, 2,6-Diaminopyridin, 2,3-Diamino-6-methoxypyridin and 3,5-Diamino-2,6-dimethoxypyridin, - Naphthalinderivate as for example 1-Naphthol, 2-Methyl-1-naphthol, 2-Hydroxymethyl-1-naphthol, 2-

Hydroxyethyl-1-naphthol, 1,5-Dihydroxynaphthalin, 1,6-Dihydroxynaphthalin, 1,7-Dihydroxynaphthalin, 1,8-Dihydroxynaphthalin, 2,7-Dihydroxynaphthalin and 2,3-Dihydroxynaphthalin,
 - Morpholinderivate as for example 6-Hydroxybenzomorpholin and 6-Aminobenzomorpholin,
 - Chinoxalinderivate as for example 6-Methyl-1,2,3,4-tetrahydrochinoxalin,
 - Pyrazolinderivate as for example 1-Phenyl-3-methylpyrazol-5-on,
 - Indolinderivate as for example 4-Hydroxyindol, 6-Hydroxyindol and 7-Hydroxyindol,
 - Pyrimidinderivate, as for example 4,6-Diaminopyrimidin, 4-Amino-2,6-dihydroxypyrimidin, 2,4-Diamino-6-hydroxypyrimidin, 2,4,6-Trihydroxypyrimidin, 2-Amino-4-methylpyrimidin, 2-Amino-4-hydroxy-6-methylpyrimidin and 4,6-Dihydroxy-2-methylpyrimidin, or
 - Methylendioxybenzolinderivate as for example 1-Hydroxy-3,4-methylendioxybenzol, 1-Amino-3,4-methylendioxybenzol and 1 (2'-Hydroxyethyl) - amino-3,4-methylendioxybenzol.

[0062] Particularly according to invention preferred Kupplerkomponenten is 1-Naphthol, 1,5, 2,7 - and 1,7-Dihydroxynaphthalin, 3-Aminophenol, 4-min CO₂ methyl phenol, 2-Amino-3-hydroxypyrimidin, resorcinol, 4-Chlorresorcin, 2-Chlor-6-methyl-3-aminophenol, 2-Methylresorcin, 5-Methylresorcin, 2,5-Dimethylresorcin and 2,6-Dihydroxy-3,4-dimethylpyridin.

[0063] At least in an other embodiment the coloring means contain one preliminary stage of a nature-analogue dye of the present invention as coloring material before product (FV). As preliminary stages of nature-analogue dyes preferred such Indole and indolines used, which at least a hydraulic XY or an amino group, preferred as substituent at the Sechrsring, to exhibit, become. These groups know other substituents inertial, z. B. in form of an etherification or esterification of the hydroxy group or an alkylation of the amino group. In a second preferred embodiment the coloring means contain at least an indol and/or a Indolinderivat.

[0064] Particularly good hair coloring materials suitable nature-analogue as preliminary stages are derivatives of the 5,6-Dihydroxyindolins of the formula (IIia),

EMI19.1

in that independently

- R₁ 1> stands for hydrogen, a C1-C4-Alkylgruppe or a C1-C4-Hydroxy-alkylgruppe,
- R₂ 2> COOH group stands also as salt with a physiological compatible cation to be present can for hydrogen or one - COOH group, whereby - ,
- R₃ 3> stands for hydrogen or a C1-C4-Alkylgruppe,
- R₄ 4> CO-R 6, in R 6 stands for hydrogen, <> a C1-C4-Alkylgruppe or a group< -> stands for a C1-C4-Alkylgruppe, and
- R₅ 5> that stands for bottom R 4 for< one> groups mentioned, as well as physiological acceptable salts of these compounds with an organic or inorganic acidic one.

[0065] Particularly preferred derivatives of the indoline are the 5,6-Dihydroxyindolin, N-Methyl-5,6-dihydroxyindolin, N-Ethyl-5,6-dihydroxyindolin, N-Propyl-5,6-dihydroxyindolin, N-Butyl-5,6-dihydroxyindolin, 5,6-Dihydroxyindolin-2-carbon-säure as well as the 6-Hydroxyindolin, the 6-Aminoindolin and the 4-Aminoindolin.

[0066] Particularly to emphasize are within this group N-Methyl-5,6-dihydroxyindolin, N-Ethyl-5,6-dihydroxyindolin, N-Propyl-5,6-dihydroxyindolin, N-Butyl-5,6-dihydroxyindolin and in particular the 5,6-Dihydroxyindolin.

[0067] As preliminary stages of nature-analogue hair coloring materials excellent suitable is further derivatives of the 5,6-Dihydroxyindols of the formula (IIib),

EMI20.1

in that independently

- R₁ 1> stands for hydrogen, a C1-C4-Alkylgruppe or a C1-C4-Hydroxyalkylgruppe,
- R₂ 2> COOH group stands also as salt with a physiological compatible cation to be present can for hydrogen or one - COOH group, whereby - ,
- R₃ 3> stands for hydrogen or a C1-C4-Alkylgruppe,
- R₄ 4> CO-R 6, in R 6 stands for hydrogen, <> a C1-C4-Alkylgruppe or a group< -> stands for a C1-C4-Alkylgruppe, and
- R₅ 5> that stands for bottom R 4 for< one> groups mentioned,
- as well as physiological acceptable salts of these compounds with an organic or inorganic acidic one.

[0068] Particularly preferred derivatives of the Indols are 5,6-Dihydroxyindol, N-Methyl-5,6-dihydroxyindol, N-Ethyl-5,6-dihydroxyindol, N-Propyl-5,6-dihydroxyindol, N-Butyl-5,6-dihydroxyindol, 5,6-Dihydroxyindol-2-carbonsäure, 6-Hydroxyindol, 6-Aminoindol and 4-Aminoindol.

[0069] Within this group to emphasize are N-Methyl-5,6-dihydroxyindol, N-Ethyl-5,6-dihydroxyindol, N-Propyl-5,6-dihydroxyindol, N-Butyl-5,6-dihydroxyindol as well as in particular the 5,6-Dihydroxyindol.

[0070] The Indolin and Indol derivatives know free bases in the coloring means according to invention both and in form of its physiological acceptable salts with inorganic or organic acidic one, z. B. the hydrochlorides, which becomes sulfates and hydrobromides, used. The indol or Indolin derivatives is in these usually in amounts of 0.05-10 Gew. - %, preferably 0.2-5 Gew. - % contain.

[0071] In an other embodiment it can be preferred according to invention to use the Indolin or Indolinderivat in coloring means in combination with at least one amino acid or an oligopeptide. The amino acid is favourable proves one [alpha] - to amino acid; whole particularly preferred [alpha] - amino acids are arginine, ornithine, lysine, serine and histidine, in particular arginine.

[0072] Beside the coloring material before products according to invention (FV) the coloring means according to invention can contain several direct dyes of the present invention in an other preferred embodiment to the Nuancierung or. Direct dyes are usually Nitrophenyldiamine, Nitroaminophenole, azo dyes, anthraquinones or Indophenole. Preferred direct dyes are those the bottom international designations and/or. Trade name HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, HC Yellow 12, Acid Yellow 1, Acid Yellow 10, Acid Yellow 23, Acid

Yellow 36, HC orange 1, disperse orange 3, Acid orange 7, HC talk 1, HC talk 3, HC talk 10, HC talk 11, HC talk 13, Acid talk 33, Acid talk 52, HC talk BN, pigment talk 57:1, HC Blue 2, HC Blue 12, disperse Blue 3, Acid Blue 7, Acid Green 50, HC Violet 1, disperse Violet 1, disperse Violet 4, Acid Violet 43, Disperse Black 9, Acid Black 1, and Acid Black 52 known compounds as well as 1,4-Diamino-2-nitrobenzol, 2-Amino-4-nitrophenol, 1,4-Bis-([beta]-hydroxyethyl)-amine CO₂ nitrobenzene, 3-Nitro-4-([beta]-hydroxyethyl)-aminophenol, 2-([2'-Hydroxyethyl)amino-4,6-dinitrophenol, 1-([2'-Hydroxyethyl)amino-4-methyl-2-nitrobenzol, 1-Amino-4-([2'-Hydroxyethyl)-amino-5-chlor-2-nitrobenzol, 4-Amino-3-nitrophenol, 1-([2'-Ureidoethyl)amino-4-nitrobenzol, 4-Amino-2-nitrodiphenylamin-2'-carboxylic acid, 6-Nitro-1,2,3,4-tetrahydrochinoxalin, 2-Hydroxy-1,4-naphthochinon, Pikraminsäure and their salts, 2-Amino-6-chloro-4-nitrophenol, 4-Ethylamino-3-nitrobenzoesäure and 2-Chloro-6-ethylamino-1-hydroxy-4-nitrobenzol.

[0073] Furthermore the agents according to invention can contain a cationic direct dye. Particularly preferred participates

(A) cationic Triphenylmethanfarbstoffe, as for example basic Blue 7, basic Blue 26, basic Violet 2 and basic Violet 14,

(B) aromatic systems, which are substituted with a quaternary group of nitrogens, as for example basic Yellow 57, basic talk 76, basic Blue 99, basic Brown 16 and basic Brown 17, as well as

(C) direct dyes, which heterocycle contain, which at least quaternary nitrogen atom exhibits, how they for example in the EP-A2-998 908 becomes taken on which in this place explicit respect, become, in the claims 6 to 11 mentioned.

[0074] Preferred cationic direct dyes of the group (C) are in particular the subsequent compounds:

EMI22.1

EMI23.1

[0075] The compounds of the formulas (DZ1), (DZ3) and (DZ5), which the also bottom designations basic Yellow 87, basic orange 31 and basic talk 51 known are, are whole particularly preferred cationic direct dyes of the group (C).

[0076] The cationic direct dyes, those the bottom trademark Arianor® sold become, are likewise according to invention whole particularly preferred cationic direct dyes.

[0077] The agents according to invention in accordance with this embodiment contain the direct dyes preferred in an amount from 0,01 to 20 Gew.-%, related to the entire coloring means.

[0078] Further the preparing according to invention can contain occurring dyes also in the nature like for example in Henna red, Henna neutral, Henna black, chamomile bloom, Sandelholz, black dye, putrid bark, Salbei, blue wood, Krappwurzel, Catechu, Sedre and alkene Anna root are contained.

[0079] It is not required that the oxidation coloring material before products or the direct dyes represent uniform in each case compounds. Rather still other components can be contained, so far these the coloring result adverse not affect or from other reasons, e.g. in the hair coloring means according to invention, under the manufacturing processes for the single dyes, in subordinate amounts, toxicological, excluded to become to have.

[0080] Concerning into the according to invention the hair coloring and -hue-average insertable dyes becomes further expressly on the Monographie CH. Zviak, The Science Of Hair Care, Chapter 7 (pages 248-250; direct dyes) as well as Chapter 8, pages 264-267; Oxidation coloring often before products), appeared as band 7 of the series "Dermatology" (Hrsg.: CH., Culnan and H. May brook), publishing house Marcel Dekker Inc., New York, Basel, 1986, as well as the "European inventory of the Kosmetik raw materials", edited of the European community, available industrie and trading venture for drugs, reform goods and toiletry registered association, Mannheim, respect taken, German in diskette form of the Federal association.

[0081] The coloring means according to invention can contain further all effect, auxiliary known for such preparing and adjuvants. In many cases the coloring means contain a surfactant at least, whereby both anionic and zwittrionisch, ampholytic, nonionic and cationic surfactants suitable are in principle. In many cases it proved however as favourable, the surfactants from anionic to select zwittrionisch or nonionic surfactants.

[0082] As anionic surfactants all are suitable for the use at the human body of suitable anionic surface-active fabrics in preparing according to invention. These are characterized by a soluble, anionic group such as z. B. a carboxylate, a sulfate, a sulfone or phosphate group and a lipophilic alkyl group with approximately 10 to 22 C-atoms. Additional ones can be contained in the molecule glycol or Polyglykolether groups, ester, ether and amide groups as well as hydroxyl groups. Examples for suitable anionic surfactants are, in each case in form the sodium, potassium and ammonium as well as of the mono, and Trialkanolammoniumsalze with 2 or 3 C-atoms in the Alkanolgruppe,

- linear fatty acids with 10 to 22 C-atoms (soaps),
- Ethercarbonsäuren of the formula R-O (CH₂-CH₂O) x-CH₂-COOH, in which R is a linear alkyl group with 10 to 22 C-atoms and x = 0 or 1 to 16,
- Acylsarcoside with 10 to 18 C-atoms in the acyl group,
- Acyltauride with 10 to 18 C-atoms in the acyl group,
- Acylsulfonate with 10 to 18 C-atoms in the acyl group,
- Sulfobetainensäuremono- und -dialkylester mit 8 bis 18 C-Atomen in der AlkylSulfobetainensäuremono-alkylpolyoxyethylester mit 8 bis 18 gruppe und C-Atomen in der Alkylgruppe und 1 bis 6 Oxyethylgruppen,
- linear Alkansulfonate with 12 to 18 C-atoms,
- linear alpha olefine sulfonates with 12 to 18 C-atoms,
- Alpha sulfo fatty acid methyl esters of fatty acids with 12 to 18 C-atoms,
- Alkyl sulfates and Alkylpolyglykolethersulfate of the formula R-O (CH₂-CH₂O) x-SO₃H, in which R is a preferred linear alkyl group with 10 to 18 C-atoms and x = 0 or 1 to 12,
- Mixtures of surface-active Hydroxysulfonate in accordance with DE-A 37 25.030,
- sulfated hydroxyalkyl polyethylene and/or Hydroxyalkylenpropylyglykolether in accordance with DE-A 37

23.354.

- Sulfonate of unsaturated fatty acids with 12 to 24 C-atoms and 1 to 6 double bonds in accordance with DE-A-39 26,344.

- Esters of the tartaric acid and citric acid with alcohols, which represent accumulation products of approximately 2-15 molecules ethylene oxide and/or propylene oxide to fatty alcohols with 8 to 22 C-atoms.

[0083] Preferred anionic surfactants are alkyl sulfates, Alkylpolyglykolethersulfate and Ethercarbonsäuren with 10 to 18 C-atoms in the alkyl group and up to 12 Glykolethergruppen in the molecule as well as in particular salts from satisfied and in particular unsaturated C8-C22-Carbonsäuren, like oleic acid, stearic acid, isostearic acid and palmitic acid.

[0084] In the frame of an embodiment of the present invention it can be preferred, if the ready for use coloring means contain at least a nichtionogenes surfactant. Nichtionogene of surfactants contain 2 as hydrophilic group. B. a group of polyole, a Polyalkylenglykolethergruppe or a combination from polyole and Polyglykolethergruppe. Such compounds are for example

- Accumulation products from 2 to 30 mole ethylene oxide and/or 0 to 5 mole propylene oxide to linear fatty alcohols with 8 to 22 C-atoms, at fatty acids with 12 to 22 C-atoms and to alkyl phenols with 8 to 15 C-atoms in the alkyl group.

- C12-C22-Fettsäuremono- und - more diester of accumulation products of 1 to 30 mole ethylene oxide at glycerol,

- C8-C22-Alkylmono- und - oligoglycoside and their ethoxylated analogues as well as

- Accumulation products castor oil hardened from 5 to 60 mole ethylene oxide to castor oils and.

[0085] Preferred nonionic surfactants are Alkylpolyglykoside of the general formula $R_1 > \text{o} (Z) X$. These compounds are characterized by the subsequent parameters.

[0086] The alkyl radical $R_1 > 6$ to 22 carbon atoms and can both linear and branched contain be. Preferred ones are primary linear and aliphatic radicals methyl-branched in 2-Stellung. Such alkyl radicals are for example 1-Octyl, 1-Decyl, 1-Lauryl, 1-Myristyl, 1-Cetyl and 1-Stearyl. Particularly preferred is 1-Octyl, 1-Decyl, 1-Lauryl, 1-Myristyl. With use of so called "Oxo alcohols" as starting materials compounds with an odd number of carbon atoms in the alkyl chain outweigh.

[0087] Useful the according to invention Alkylpolyglykoside knows for example only a certain alkyl radical $R_1 > 1$ contained. Usually these compounds become however prepared on the basis of natural fats and oils or mineral oils. In this case mixtures the corresponding starting compounds lie and/or as alkyl radicals R. the corresponding respective workup of these compounds forwards.

[0088] Particularly preferred is such Alkylpolyglykoside, with those $R_1 > 1$

- essentially from C8 and C10-Alkylgruppen,

- essentially from C12 and C14-Alkylgruppen,

- essentially from C8 to C16-Alkylgruppen or

- consists essentially of C12 to C16-Alkylgruppen.

[0089] As sugar component Z arbitrary mono or oligosaccharides used can become. Usually sugar with 5 becomes and/or, 6 carbon atoms as well as the corresponding oligosaccharides used. Such sugar is for example glucose, fructose, galactose, arabinose, ribose, xylose, Lyxose, all eye, old rose, mannose, Glucose, Idose, valley eye and sucrose. Preferred sugar components are glucose, fructose, galactose, arabinose and sucrose; Glucose is particularly preferred.

[0090] Useful the according to invention Alkylpolyglykoside contains in the section 1.1 to 5 sugar moieties.

Alkylpolyglykoside with x-values from 1,1 to 1.6 are preferred. Whole particularly preferred is Alkylglykoside, with which x amounts to 1.1 to 1.4.

[0091] The Alkylglykoside can serve beside their Tensidwirkung also to improve the fixation of smell components on the hair. The person skilled in the art will thus if an effect of the perfume oil on the hair desired, going beyond the durations of the hair treatment, preferred to this substance class as other ingredient of the erfindungsgemäßen preparing will fall back.

[0092] Also the alkoxylated homologous ones the Alkylpolyglykoside mentioned can become used according to invention. These homologous ones can contain average up to 10 ethylenoxid and/or propylene oxide units per Alkylglykosideinheit.

[0093] Further, in particular as Co surfactant, zwitterionic surfactants can become used. As zwitterionic surfactants such surface-active compounds referred become, those in the molecule at least a quaternary ammonium group and at least one -COO⁻ (-)- or -SO₃⁻ (-)- group inertial. Particularly suitable zwitterionic surfactants are the so called betaines like the N-alkyl-n, N-dimethylammonium-glycinate, for example Kokosalkyl dimethylammonium glycinate, N-acyl-aminopropyl-n, N-dimethylammoniumglycinate, for example Kokosacylaminoethyl dimethylammoniumglycinate, and 2-Alkyl-3-carboxyethyl-3-hydroxyethyl-imidazoline with in each case 8 to 18 C-atoms in the alkyl or acyl group as well as the Kokosacylaminoethylhydroxyethylcarboxymethylglycinate. A preferred zwitterionic surfactant is that the bottom INCI designation Cocamidopropyl of betaines known fatty acid amide derivative.

[0094] As Co surfactant suitable are ampholytic surfactants likewise in particular. Bottom ampholytic surfactants become such surface-active compounds understood, which are except a C8-C18-Alkyl or an acyl group contained in the molecule at least a free amino group and at least one -COOH or -SO₃H-Gruppe and to the formation of inner salts capable. Examples for suitable ampholytic surfactants are N-Alkylglycine, N-Alkylpropionsäuren, N-Alkylaminobuttersäuren, N-Alkyliminodipropionsäuren, N-Hydroxyethyl-N-alkylamidopropylglycine, N-Alkyltaurine, N-Alkylsarcosine, 2-Alkylaminopropionsäuren and Alkylaminoessigsäuren with about in each case 8 to 18 C-atoms in the alkyl group. Particularly preferred ampholytic surfactants are the N-Kokosalkylaminopropionat, the Kokosacylaminoethylaminopropionat and the C12-18-Acylsarcosine.

[0095] The Esterquats and the Amidoamine become according to invention used as cationic surfactants in

particular such of the type of the quaternary ammonium compounds.

[0096] Preferred quaternary ammonium compounds are ammonium halides, in particular chlorides and bromides, like alkyl tri methyl ammonium chloride, Dialkyldimethylammoniumchloride and tri alkyl methyl ammonium chloride, z. B. Cetyltrimethylammoniumchlorid, Stearyltrimethylammoniumchlorid, Distearyltrimethylammoniumchlorid, Lauryldimethylammoniumchlorid, Lauryldimethylbenzylammoniumchlorid and Tricetyltrimethylammoniumchlorid, as well as those the bottom INCI designations Quaternium-27 and Quaternium-83 known Imidazolium compounds. The prolonged alkyl chains of the surfactants specified above exhibit preferred 10 to 18 carbon atoms.

[0097] With Esterquats it concerns known fabrics, who contain both at least one ester function and at least a quaternary ammonium group as structural element. Preferred Esterquats is quaternierte ester salts of fatty acids with triethanolamine, quaternierte ester salts of fatty acids with Diethanolalkylaminen and quaternierten ester salts of fatty acids with 1,2-Dihydroxypropyldialkylaminen. Such products become the for example bottom trademarks Stepatex< (R)>, Dehyquart< (R)> and Armocare< (R)> sold. The products Armocare< (R)> VGH-70, a N, N-Until (2-Palmitoyloxyethyl) dimethylammoniumchlorid, as well as Dehyquart< (R)> F-75 and Dehyquart< (R)> AU-35 are examples for such Esterquats.

[0098] The Alkylamidoamine becomes usually prepared by amidation natural or synthetic fatty acids and fatty acid cuts with Dialkylaminoamine. One particularly according to invention suitable compound from this group of substances places that to the bottom designation Tegamid< (R)> S 18 Stearamidopropylmethylamin available in the trade.

[0099] Other useful according to invention cationic surfactants represent the quaternized protein hydrolysates.

[0100] Likewise according to invention suitable is cationic silicone oils as for example in the trade the available products Q2-7224 (manufacturer: Dow Corning; a stabilized Trimethylsilylamodimethicon), Dow Corning 929 emulsion (a contained hydroxyl-revision modification-NO-modified silicone, which becomes also referred as Amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) as well as Abilc< (R)> - Quat 3270 and 3272 (manufacturers: Th. Goldschmidt; diquaternäre polydimethylsiloxanes, Quaternium-80).

[0101] An example for a quaternary sugar derivative insertable as cationic surfactant represents the commercial product Glucquat< (R)> to 100, in accordance with INCI nomenclature a "Lauryl methyl Glucoeth-10 hydroxypropyl Dimonium of chlorides".

[0102] With the compounds with alkyl groups, used as surfactant, it can concern in each case uniform substances. It is however usually preferred to proceed with the preparation of these fabrics from native vegetable or animal raw materials so that one receives substance mixtures with different alkyl chain lengths dependent of the respective raw material.

[0103] With the surfactants, which represent accumulation products of ethyl and/or propylene oxide to fatty alcohols or derivatives of these accumulation products, both products with a "normal" homologous distribution and such with a concentrated homologous distribution used can become. Bottom "normal" homologous distribution become understood, which one receives during the conversion from fatty alcohol and alkylene oxide using alkali metals, thereby mixtures of homologous ones, alkali metal hydroxides or alkali metal alcoholates as catalysts. Concentrated homologous distributions become if for example hydrotalcites, obtained against it, alkaline earth metal salts of Ehercarbonsäuren, become alkaline earth metal oxides, -hydroxides or -alcoholates as catalysts used. The use of products with concentrated homologous distribution can be preferred.

[0104] In an other preferred embodiment the agents contain a reducing agent at least of the present invention. Examples for preferred according to invention reducing agents are sulfites, ascorbic acid, ISO ascorbic acid, thiols, Thioglykolsäure and their derivatives, Natriumthionit, alkali metal CIT advice salts and N-acetyl-L-cysteine whole one particularly preferred reducing agents are sulfites, in particular sodium sulfite, alkali metal CIT advice salts, in particular sodium citrate, and N-acetyl-L-cysteine. N-acetyl-L-cysteine and sodium sulfite are whole particularly preferred reducing agents.

[0105] Furthermore the coloring means according to invention know other effect, auxiliary and additives, as for example

- nonionic polymers as for example Vinylpyrrolidon/Vinylacrylat copolymers, polyvinylpyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes,
- cationic polymers like quaternized cellulose ethers, polysiloxanes with quaternary groups, Dimethyldiallylammoniumchlorid polymers, acrylamide Dimethyldiallylammoniumchlorid copolymers, with Diethylsulfat Dimethylaminoethylmethacrylat vinylpyrrolidonecopolymers, Vinylpyrrolidon Imidazoliummethochlorid copolymers and quaternierter polyvinyl alcohol quaternierte,
- anionic polymers as for example polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/Crotonsäure copolymers, Vinylpyrrolidon/Vinylacrylat copolymers, vinyl acetate/Butylmaleat/Isobornylacrylat copolymers, Methylvinylether/Maleinsäureanhydrid copolymers and acrylic acid/Ethylacrylat/N tert. Butyl acrylamide terpolymers,
- Thickeners such as agar agar, Guar Gum, alginates, Xanthan Gum, gum Arabic, Karaya gum, Johannisbrotkernmehl, Leinsamengummen, dextrins, cellulose derivatives, z. B. Methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, strength fractions and derivatives such as amylose, amylopectin and dextrins, clays such as z. B. Bentonite or full-synthetic hydraulic colloids like e.g. Polyvinyl alcohol,
- Strukturanten such as maleic acid and lactic acid,
- hair-conditioning compounds such as phospholipids, for example Sojalecithin, egg-Lecitin and Kephaline,
- Protein hydrolysates, in particular Elastin, kollagen, Keratin, milk protein, Sojaprotein and wheat protein hydrolysates, their condensation products with fatty acids as well as quaternized protein hydrolysates,
- Perfume oils, Dimethylisoborbid and cyclodextrins,
- Solvents and - mediators such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- fibrous structure-improving active ingredients, in particular mono- and oligosaccharides as for example glucose,

- galactose, fructose, fruit sugar and lactose,
- quaternierte amines such as Methyl- 1- alkylamidoethyl- 2- alkylimidazolium- methosulfat
- Defoamers such as Silikone,
- Dyes to the Anfärben of the agent,
- Anti shed active substances such as Piroctone Olamine, zinc Omadine and Climbazol,
- Light- protectives, in particular derivatized benzophenones, Zimtsäure derivatives and triazines,
- Substances for adjustment the pH value, as for example conventional acidic ones, in particular benefit- acidic and bases,
- Active ingredients such as Allantoin, Pyrrolidincarbonsäuren and their salts as well as Bisabolol,
- Vitamins, Provitamine and Vitaminvorstufen, in particular such of the groups A, B3, B5, B6, C, E, F and H,
- Plant extracts like the extracts from green tea, oak crust, Brennessel, Hamamelis, hop, chamomile, Klettenwurzel, box stem, white thorn, lime tree blooms, almond, aloe Vera, Fichtennadel, Roskastanie, Sandelholz, Wacholder, coconut, Mango, apricot, Limone, wheat, Kiwi, melon, orange, grapefruit, Salbei, Rosmarin, Birke, Malve, meadow foam herb, Quendel, sheep sheaf, Thymian, Melisse, Hauhechel, Huflattich, Eibisch, Meristem, Ginseng and ginger root.
- Cholesterol,
- Consistency givers such as sugar esters, polyol esters or Polyalkylether,
- Fats and wax such as whale advice, beeswax, Montanwachs and paraffins,
- Fettsäurealkanolamide
- Complexing agents such as EDTA, NTA, [beta] - alanine- this- victory- acidic and phosphonic acids,
- Pouring and penetration materials such as glycerol, Propylenglykolmonomethylether, carbonates, hydrogencarbonates, guanidines, ureas as well as primary, secondary and tertiary phosphates,
- Opacifiers such as latex, Styrol/ PVP and styrene/ acrylamide copolymers
- Perl gloss means such as ethyl glycol mono and - PEG- 3- distearat as well as distearat,
- Pigments,
- Antikorrosiva like if necessary hydrated SiO₂- Verbindungen
- Stabilizing agents for Wasserstoffperoxid and other oxidizing agents,
- Propellants such as propane butane mixtures, N₂O, dimethyl ether, CO₂ and air as well as
- Antioxidantien
- Reducing agents, like ascorbic acid, sulfites, N- acetyl- cysteine and thiols contained.

[0106] Concerning other optional components as well as the used amounts of these components known pertinent handbooks, z become express on those the person skilled in the art. B. Kh. Schrader, bases and prescriptions of the cosmetics, 2. Edition, Hüthig book publishing house, Heidelberg, 1989, referred.

[0107] A second subject- matter of the present invention are two- component means to the coloration of keratinischer fibers, existing out

- a first component (c1), contained at least one coloring material before product (FU), and
- a second component (K2), contained at least one active substance complex (A), existing
- from an active ingredient (A1), which selected is from Sericin and/ or Sericinhydrolysaten and/ or their derivatives and/ or their mixtures, and
- an active ingredient (a2), which selected is from Fibroin and/ or its hydrolysates and/ or their derivatives and/ or mixtures from it,

whereby at least one of the two components contains at least an amphoteric polymer (AP).

[0108] At least in the frame both components (c1) and (K2) an amphoteric polymer (AP) contain of a preferred embodiment of this subject- matter of the present invention. It can be thereby whole particularly preferred, if the components (c1) and (K2) the same amphoteric polymer (AP) contain.

[0109] The two- component means according to invention become immediate combined before the application a ready for use application preparation, which subsequent on the hair applied becomes.

[0110] The actual oxidative coloration of the fibers can take place in the frame of this subject- matter of the present invention with atmospheric oxygen.

[0111] Preferred one becomes however a chemical oxidizing agent used, particularly if is desired beside the coloration a Aufhelleneffekt at human hair.

[0112] A third subject- matter of the present invention is therefore a three- component means to the coloration of keratinischer fibers, existing out

- a first component (c1), contained at least one coloring material before product (FU),
- a second component (K2), contained at least one active substance complex (A), existing
- from an active ingredient (A1), which selected is from Sericin and/ or Sericinhydrolysaten and/ or their derivatives and/ or their mixtures, and - an active ingredient (a2), which selected is from Fibroin and/ or its hydrolysates and/ or their derivatives and/ or mixtures from it, and
- a third component (K3), contained at least an oxidizing agent,

whereby at least one of the two components (c1) or (K2) at least an amphoteric polymer (AP) contains.

[0113] As oxidizing agents come persulfates, chlorites and in particular hydrogen peroxide or its accumulation products at urea, melamine as well as sodium borate into question. In the frame of this subject- matter of the present invention the ready for use product becomes obtained by mixture of the three components immediate before the application on the hair.

[0114] If an extreme clarification of the natural coloration of the keratinischen fibers is to take place in frames of the coloration of the fibers, then the application preparation from coloring cream and oxidizing agent preparation (usually hydrogen peroxide solution) a so called booster becomes added. These usually powdered formulated agents contain usually as important component a solid Peroxoverbindung. The selection of these Peroxoverbindung is subject in principle to no limitations; conventional, the person skilled in the art known Peroxoverbindungen are for example Ammoniumperoxisulfat, Kaliumperoxisulfat, Natriumperoxisulfat,

ammonium persulfate, potassium persulfate, sodium persulfate, Kaliumperoxydiphosphat, percarbonates such as magnesium percarbonate, peroxides such as barium peroxide as well as perborates, urea peroxide and Melaminperoxid. Bottom this Peroxoverbindungen, which is also in combination used to become to be able, according to invention the inorganic compounds preferred. Particularly preferred is the Peroxydisulfate, in particular combinations from at least two Peroxydisulfaten. In addition, lately methods became developed, became used with which at site of the Peroxoverbindungen particular ammonium salts and salt combinations. It is referred in this place explicit to the EP-609 796A2 and the DE-196 30 453A1.

[0115] According to invention the coloring means can become also together with a catalyst on the hair applied, that the oxidation of the coloring material before products, e.g. by atmospheric oxygen, activated. Such catalysts e.g. are. Metal ions, iodides, quinones or certain enzymes.

[0116] Suitable metal ions are for example Zn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{4+} , $left < + >$, Mg^{2+} , approx. $< 2+ >$ and aluminium $< 3+ >$. Particularly suitable is thereby Zn^{2+} , Cu^{2+} and Mn^{2+} . The metal ions can become in principle in the form of any, physiological acceptable salt or in form of a complex compound used. Preferred salts are the acetates, sulfates, halides, lactates and tartrates. By use of these metal salts both the formation of the coloration accelerated and the color nuance can become targeted affected.

[0117] Suitable enzymes e.g. are. Peroxidases, which can strengthen the effect of small amounts at hydrogen peroxide significant. Further such enzymes are according to invention suitable, which oxidize by atmospheric oxygen the oxidation coloring material before products direct, as for example the laccases, or in situ small amounts hydrogen peroxide produce and the oxidation of the coloring material before products biocatalytic in this way activate. Particularly suitable catalysts for the oxidation of the dye precursors are the so called 2-Elektronen-Oxidoreduktasen in combination with the substrates specific for it, e.g.

- Pyranose oxidase and e.g. D glucose or galactose,
- Glucose oxidase and D glucose,
- Glycerin oxidase and glycerol,
- Pyruvat oxidase and Benztraubensäure or their salts,
- Alcohol oxidase and alcohol (MeOH, EtOH),
- Lactat oxidase and lactic acid and their salts,
- Tyrosinase oxidase and tyrosine,
- Uricase and uric acid or their salts,
- Cholin oxidase and choline,
- Amino acid oxidase and amino acids.

[0118] The agents/components according to invention contain the active ingredients preferred in a suitable aqueous, alcoholic or aqueous-alcoholic carrier. To purposes of the hair colouring are such carriers for example creams, emulsions, gels or also tensidhaltige foaming solutions, as for example shampoos, foam aerosols or other preparing, which are suitable for the application on the hair. In addition, it is more conceivable to formulate or the several preparing according to invention a powdered also tablet förmig or.

[0119] Bottom aqueous-alcoholic solutions are in the sense of the present invention aqueous solutions contained 3 to 70 Gew. - % of a C1-C4-Alkohols, in particular ethanol and/or. Isopropanol to understand. The agents according to invention can contain additional other organic solvents, as for example Methoxybutanol, benzyl alcohol, Ethylglykyl or 1,2-Propylenglykol. Preferred ones are thereby all water-soluble organic solvents.

[0120] The resultant in each case ready for use hair coloring preparation should exhibit a preferred pH value within the range of 6 to 12. Particularly preferred is the application of the hair coloring means in a weak alkaline environment. The application temperatures can in a range between 15 and 40 [deg.]C lie. After an induction period from 5 to 45 minutes the hair coloring means becomes remote by rinsing out the hair which can be colored. Washing afterwards with a shampoo entfärlt, if a strong tensidhaltiger carrier, e.g. a coloring shampoo, used became.

[0121] In particular with severe colorable hair can the preparation with the coloring material before products in working, without previous mixture with the oxidation component on the hair applied become. After a short working period from 20 to 30 minutes then - if necessary after an intermediate flushing - the oxidation component becomes applied. After an other short working period from 10 to 20 minutes rinsed is then nachschampooniert and gewünschtenfalls. With this embodiment the corresponding agent becomes to a pH value from approximately 4 to 7 adjusted in accordance with a first variant, with which previous applying of the coloring often before products is to cause a better penetration into the hair. In accordance with a second variant first an air oxidation becomes desired, whereby the applied agent exhibits a preferred pH value from 7 to 10. During the subsequent accelerated Nachoxidation can be the use of acidic adjusted Peroxydisulfat solutions as oxidizing agents preferred.

[0122] A fourth subject-matter of the present invention is a method to the coloration of keratinischer fibers, whereby one of the agents according to invention becomes rinsed subsequent for an impact time left and on the fibers applied, there.

Embodiment

1 preparation of the prescriptions

[0123] The subsequent prescriptions prepared became:

1.1 care component with silk proteins

EMI36.1

[1] silk protein hydrolysate (approx. 3.9 to 5.3 Gew. - % active ingredient content; INCI designation: Sericin) (Pentapharm)

[2] Collagenhydrolysat (approx. 5 to 8 Gew. - % active ingredient content; INCI designation: Hydrolyzed Silk) (RITA corporation)

[3] disodium salt of the 5-Amino-4-hydroxy-3-phenylazo-2,7-naphthalindisulfonsäure (INCI designation:

C1= 17200)

{ 4 } (INCI designation: C1= 47005 (Yellow 10))

{ 5 } delayed soluble hydroxyethyl cellulose (approx. 95% active ingredient content; INCI designation: Hydroxyethyl cellulose) (Hercules)

1,2 care component with silk proteins and amphoteric polymer

EMI37.1

{ 6 } approx. 20Gw. - % active ingredient content in waters; INCI designation: Acrylamidopropyltrimonium of chlorides/Acrylates copolymer (stick-live)

1,3 coloring material preparation

EMI38.1

{ 7 } Laurylmyristylethersulfat sodiumsalt (approx. 68% to 73% Aktivsubstanzgehalt; INCI designation: Sodium Myreth of sulfates) (Cognis)

{ 8 } Laurylalkohol-4,5-EO-Essigsäure-Natrium-Salz (at least. 21% active ingredient content; INCI designation: Sodium Laureth-6 of carboxylates) (CChem y)

{ 9 } C-fatty alcohol (INCI designation: Cetearyl Alco-get) (Cognis)

{ 10 } C-fatty alcohol (INCI designation: Coconut Alco-get) (Cognis)

{ 11 } Alkylpolyglucosid Ölsäuremonoglycerid mixture (INCI designation: Coco glucosides, Glycerol of oleates, Aqua (Water); approx. 32% to 35% water content) (Cognis)

{ 12 } 2-Octyldodecylalkohol (INCI designation: Octyldodecanol) (Cognis)

{ 13 } C-fatty alcohol with approx. 12-EO-Einheiten (INCI designation: Ceteareth-12) (Cognis)

{ 14 } Cetylstearylalkohol with approx. 20-EO units (INCI designation: Ceteareth-20) (Cognis)

{ 15 } 1-Hydroxyethan-1,1-diphosphonsäure (INCI designation: Etidronic Acid) (Cognis)

{ 16 } approx. 40% active ingredient (INCI designation: Sodium of silicates) (HENKELS)

1,4 oxidizing agent preparation

EMI39.1

{ 17 } Laurylthersulfat sodiumsalt (INCI designation: Sodium Laureth of sulfates, approx. 26,5% active ingredient) (Cognis)

{ 18 } nichtionogene silicone emulsion (INCI designation: Dimethicone, approx. 10% active ingredient) (Dow Corning)

{ 19 } acid-contained, crosslinked acrylic copolymer (INCI designation: Acrylates copolymer, approx. 28% active ingredient) (Rohm&Haas)

2 Ausfärbung von Strähnen

[0124] The coloring creams F1 to F3 in accordance with table 1 became mixed in the ratio 1:1 with the oxidizing agent preparation (see point 1,4). In each case 8g of the resultant application preparation became on 20 Naturhaarsträhnen (2g, Alkenco 6634, simple blondiert with commercial product Poly blond one <(R)> Medium) applied and 30min with room temperature leave there. Subsequent ones became the hairs with water thorough purged.

[0125] After rinsing out the wet combing barness of the Strähnen determined became more immediate. In the frame of these measurements the combing resistance determined, i.e., becomes the force, which is required, in order to pull a measuring comb by the Haarsträhne. As reference in each case the measurement value of the Strähnen before the dyeing process (0% reduction of the wet combing strength) served. The results are in table 1 assembled.

Table 1

EMI40.1

[0126] The results show significant that the prescriptions according to invention with silk proteins and an amphoteric polymer (F1 and F2) are superior to the comparison prescriptions with amphoteric polymer alone (F3) regarding the wet combing barness significant (higher reduction of the wet combing strength).

3 Ausfärbung at test persons

[0127] The coloring creams according to invention F1 and F2 became beyond that in the half side test against the coloring cream F3 in the Haarstudio tested. In addition the hairs from in each case 40 models became to two pages clever ELT. On the page the prescription according to invention (60ml F1 and/or 60ml F2 in each case in the mixture with 30ml oxidizing agent preparation in accordance with point 1,4) became and on the other page the comparison prescription (60ml F3 in the mixture with 60ml oxidizing agent preparation in accordance with point 1,4) applied. Otherwise the hairs of the test persons became identical treated. The Ausfärbung made for 30 min with room temperature. Subsequent ones became the hairs with waters thorough rinsed and dried. The judgment became independent in each case by 3 persons of the technical personnel performed. The judgments are in table 2 assembled.

Table 2

EMI41.1